



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

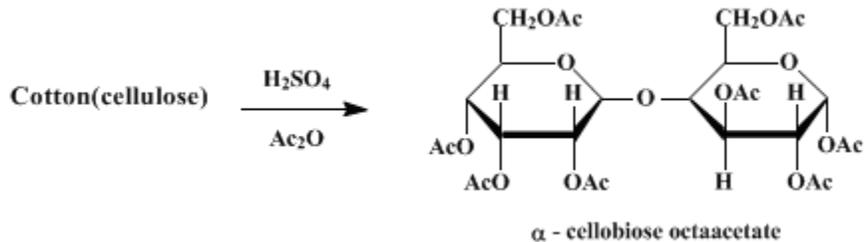
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The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## **$\alpha$ -CELLOBIOSE OCTAACETATE**



Submitted by Géza Braun

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### 1. Procedure

In a 1-l. wide-mouthed bottle with a glass stopper, 400 cc. of **acetic anhydride** is cooled to  $-10^\circ$  in a freezing mixture and 36 cc. of concentrated **sulfuric acid** is added at once with constant stirring. The temperature of the solution rises to about  $20^\circ$ . The bottle is removed from the freezing mixture, and 20 g. of absorbent cotton (**Note 1**) is worked into the liquor immediately with a heavy glass rod. With constant stirring, the bottle is warmed in a water bath maintained at  $60^\circ$  until the temperature of the mixture reaches  $45^\circ$  (about ten minutes), and then it is removed and the temperature is kept from rising above  $55^\circ$  by suitable cooling with running water, stirring being continued throughout (**Note 2**). After about twenty minutes (total) the mixture becomes thin; at this point it is cooled to  $50^\circ$  and a second 20-g. portion of cotton is added with stirring, the temperature again being kept from rising above  $55^\circ$ . The process of cooling to  $50^\circ$  and adding 20 g. of cotton is repeated at intervals of about ten minutes until 100 g. of cotton in all has been introduced. After the final addition stirring is continued until the mixture becomes thin (about ten minutes); then the bottle is stoppered and heated in a bath maintained at  $50^\circ$  for one hour, during which time the cotton dissolves completely to a thin, light brown syrup. The stoppered container is kept in an oven at  $35^\circ$  for seven days.

The solution darkens to a deep wine-red color, and  **$\alpha$ -cellobiose octaacetate** begins to crystallize on the second day (**Note 3**). After seven days at  $35^\circ$  the semi-crystalline mass is stirred into 0 l. of cold water. With good stirring the flocculent precipitate of  **$\alpha$ -cellobiose octaacetate** and cellulose-dextrin acetates soon becomes crystalline; after standing for one to two hours the solid is collected on a 12.5-cm. Büchner funnel, washed free from acid with cold water, and drained thoroughly. The moist product, weighing about 250 g., is triturated with 250 cc. of warm **methyl alcohol**, and, after cooling to room temperature, the undissolved solid is collected on a 7-cm. Büchner funnel, washed with three 50-cc. portions of **methyl alcohol**, and dried at  $40^\circ$ . The yield of fairly pure  **$\alpha$ -cellobiose octaacetate** is 69–74 g. For purification it is dissolved in 300 cc. of **chloroform** and the solution is filtered by suction into a dry receiver through a pad prepared by dusting **Norite** onto a Büchner funnel and washing the funnel with alcohol. The **chloroform** solution is filtered while the pad is still wet with alcohol, and the filter is washed at once with 100 cc. of **chloroform** without interruption in the filtration. The colorless filtrate is concentrated at reduced pressure until the acetate begins to crystallize (about 250 cc.), the crystals are redissolved by warming, and the solution is poured into 750 cc. of warm **methyl alcohol**. The acetate begins to crystallize at once as small needles which eventually form a thick paste. The mixture is cooled to  $0^\circ$  with stirring, and after about one hour the material is collected, washed with 100 cc. of **methyl alcohol**, and dried at  $40^\circ$ . The yield of colorless  **$\alpha$ -cellobiose octaacetate**, m.p.  $220$ – $222^\circ$ ,  $[\alpha]_D^{20} + 41.6^\circ$ , is 65–69 g. (35–37 per cent of the theoretical amount, assuming that the cotton contains 10 per cent of moisture) (**Note 4**), (**Note 5**), and (**Note 6**).

For further purification a solution of the material in 350 cc. of **chloroform** is clarified if necessary and poured into 750 cc. of **methyl alcohol**, and the mixture is cooled to  $0^\circ$ . The yield of the pure acetate, m.p.  $225$ – $226^\circ$ ,  $[\alpha]_D^{20} + 42.5^\circ$ , is 61–65 g. The constants are not altered by further crystallizations.

## 2. Notes

1. Pure commercial cotton or filter paper may be used. These materials ordinarily contain 7–10 per cent of moisture.
2. Effective stirring and careful control of the reaction are essential to obtain good yields. If left uncontrolled, the temperature may rise quickly above 100° with considerable decomposition.
3. The crystallization is accelerated by scratching the walls of the jar or by seeding. Seed is obtained easily by pouring a small portion of the reaction mixture into a large amount of water; the precipitate is separated, treated with alcohol, and dried at 40°.
4. In earlier experiments a temperature of 30–40° was maintained during the addition of the cotton (which then required more time), and the acetolysis was allowed to proceed at room temperature for six days. The yield of product melting at 220–222° was 50–56 g., but rose to 62–70 g. when the period of digestion was extended to eight days.
5. The quantities can be doubled without change in the procedure or the percentage yield.
6. Pringsheim's method<sup>1</sup> of isolating the acetate gives equally good results. Instead of pouring the acetolysis mixture into water, it is kept at 0° for one to two days and the crystalline material is collected on a large Büchner funnel and washed with 50 cc. of ice-cold [acetic anhydride](#). Cellulose-dextrin acetates and other by-products pass into the filtrate. The crude mass is digested with 200 cc. of warm [methyl alcohol](#), collected, and crystallized from [chloroform-alcohol](#) as above. The yield is 65–68 g., m.p. 220–222°.

## 3. Discussion

The preparation of [α-cellobiose octaacetate](#) by the acetolysis of cellulose was discovered by Franchimont,<sup>2</sup> and the process has been studied carefully by a number of other investigators.<sup>1, 3, 4, 5</sup> The observations of Freudenberg<sup>4</sup> and Klein<sup>5</sup> were particularly useful in developing the present procedure.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 122](#)

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## References and Notes

1. Pringsheim and Merkatz, *Z. physiol. Chem.* **105**, 173 (1919).
2. Franchimont, *Ber.* **12**, 1941 (1879).
3. Skraup and König, *Monatsh.* **22**, 1011 (1901); Maquenne and Goodwin, *Bull. soc. chim.* (3) **31**, 854 (1904); Schliemann, *Ann.* **378**, 366 (1911); Ost, *ibid.* **398**, 332 (1913).
4. Freudenberg, *Ber.* **54**, 767 (1921).
5. Klein, *Z. angew. Chem.* **25**, 1409 (1912).

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## Appendix

### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Cellulose-dextrin acetates

cellulose

[sulfuric acid](#) (7664-93-9)

methyl alcohol (67-56-1)

acetic anhydride (108-24-7)

chloroform (67-66-3)

Norite (7782-42-5)

chloroform-alcohol

$\alpha$ -Cellobiose octaacetate (5346-90-7)